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JUN 78 G F KINNEY, R G SEWELL

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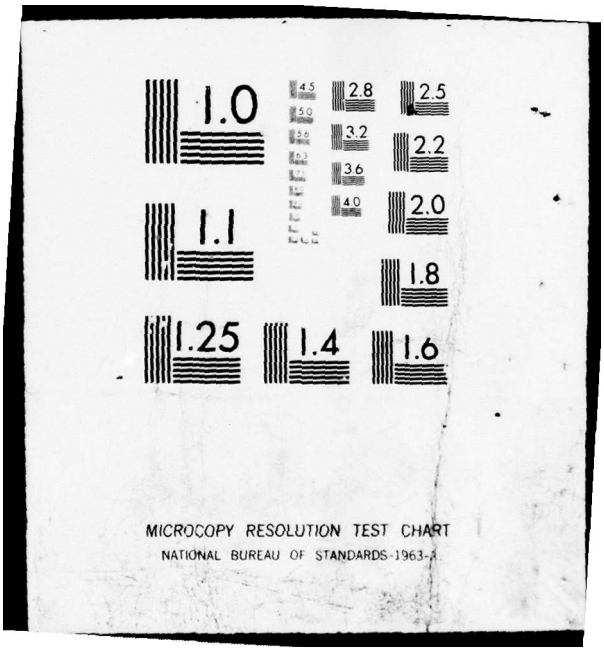
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Critical Injection Velocities for Ignition

by
G. F. Kinney
U.S. Naval Postgraduate School
and
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Naval Weapons Center

JUNE 1978

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FOREWORD

This study examines the behavior of selected combustible materials which have been forcibly injected into a confined volume of air. Theoretically calculated values for the injection velocities are reported which further provide a basis for comparisons and modifications.

This investigation was performed during fiscal year 1978 and supported jointly by Director, Navy Laboratory Programs Task R000 01 01, and NavAir Task WF32-395.

This report has been prepared primarily for timely presentation of information. Although care has been taken in the preparation of the technical material presented, conclusions drawn are not necessarily final and may be subject to revision.

Approved by
E. B. ROYCE, *Head*
Research Department
9 June 1978

Under authority of
W. L. HARRIS
RAdm., U. S. Navy
Commander

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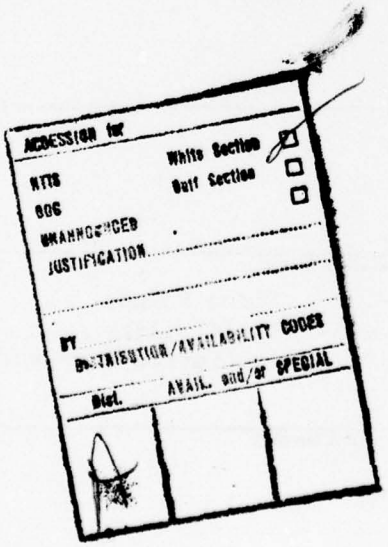
(U) *Critical Injection Velocities for Ignition,* by G. F. Kinney and R. G. S. Sewell. China Lake, Calif., Naval Weapons Center, June 1978. 18 pp. (NWC TP 6038, publication UNCLASSIFIED.)

(U) Forcible injection of combustible material into a closed volume of air can increase its temperature substantially either by molecular impaction on a blunt face of an object or by its kinetic energy loss on sudden deceleration. Injection velocities required to produce ignition temperatures by each mechanism have been computed for a variety of combustible and explosive materials. The two diverse methods of computation are in rough agreement, with representative velocities for ignition being perhaps 10^3 m/s or somewhat less, corresponding to Mach numbers of about 2 1/2. Injection velocities required for the prompt initiation of the explosion of an explosive fuel are rather comparable, and delayed initiation can occur with somewhat lesser velocities. Calculations are all speculative in nature, but they provide a solid basis for comparison of fuels and for subsequent refinement by data from experimental results.



INTRODUCTION

Forcible injection at high velocity of combustible material into a confined volume of gas can cause it to become ignited, and its subsequent combustion can generate a destructive internal explosion. One mechanism for such ignition is molecular impaction. Here the relative velocity between an object and the confined air creates a thin film of hot compressed gas at stagnation temperature and pressure on its leading face. This high velocity can readily cause ignition and subsequent combustion. An example of the impaction effect is shown by a meteorite where the temperature rise at the leading face causes incandescence.

Self-ignition of an injected fuel also may result from a conversion of kinetic energy to internal energy by rapid deceleration, so causing fuel temperature to increase to the self-ignition point. This energy-caused ignition is somewhat analogous to ignitions in a diesel engine, except that there energy input is through adiabatic compression rather than rapid deceleration.

Injection ignition effects, however, are probably more complex than these simplified mechanisms indicate. Thus material on the leading face of a particle could be volatilized by the stagnation temperature, then sudden deceleration of dispersed material gives a further temperature rise that leads to ignition and combustion.

Reported here are theoretically calculated values for the injection velocities leading to spontaneous ignition with subsequent combustion and associated internal explosion for selected combustible materials. Also reported are the velocities calculated for raising the temperature of a material to its flash point where ignition by a spark of flame can occur. The velocities necessary to initiate both prompt and delayed explosion of explosive fuels are also reported. All these are necessarily speculative in nature and so may represent oversimplified analyses. Nevertheless, the calculations provide a basis for comparisons and for possible modifications to correct for inherent inadequacies.

AUTOIGNITION TEMPERATURES FOR COMBUSTIBLE MATERIALS

Combustible materials become self-ignited when warmed to a sufficiently high temperature, one termed the autoignition temperature, or

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perhaps simply the ignition temperature. Ignition occurs as the rate of energy release by oxidation exceeds the rate of heat losses. The autoignition process is not simple, however, for it involves an induction time that decreases with increasing exposure temperature.[1] In measurement of an autoignition temperature it is important to avoid the effects of preliminary slow oxidation at lower temperatures. One method of measurement is by rapid adiabatic compression to test temperature, as in a modified internal combustion engine. Another is by mixing separately preheated fuel and air streams.

Autoignition temperatures, however, are not true properties of combustible materials but only test-dependent parameters. Thus, results from different sources seldom agree exactly. The values utilized here have been compiled from three sources, one credited to the Bureau of Mines,[2] another to the Associated Mutual Fire Insurance Companies,[3] plus the extensive tables of the Fire Protection Handbook.[4] The somewhat uncertain and test-dependent nature of autoignition temperatures is illustrated by those reported for amyl alcohol which, respectively, are 427°C, 327°C, and 300°C, with an average of 351°C, as used here.

The chemical nature of a combustible affects its autoignition temperature, but not in a well-defined way. Thus, autoignition temperatures for the normal hydrocarbons decrease with increasing chain length,[5] as for example, from 425°C for n-butane, C_4H_{10}, to 227°C for n-octane, C_8H_{18}. It also increases with chain branching, as from 227°C for normal octane to 447°C for the iso-octane 2,2,4 trimethylpentane. It appears that for motor fuels, as might be expected, there is a relation between autoignition temperature and antiknock rating. Other chemical factors such as the introduction of oxygen into a molecule also can be important. Thus the value 425°C for n-butane, C_4H_{10}, is decreased to 186°C for diethyl ether, $C_4H_{10}O$. But it does not seem possible to formalize such correlations.

All combustibles, both volatile and nonvolatile, show autoignition temperatures. Furthermore, this ignition process does not depend on

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[1] D. S. Vermeer, J. W. Meyer, and A. K. Oppenheim, "Auto-ignition of Hydrocarbons," *Combustion and Flame*, Vol. 18, No. 3 (1972) pp. 327-336.

[2] *Chemical Engineers' Handbook*, J. H. Perry, Editor, McGraw-Hill Book Company, New York (various editions).

[3] *Handbook of Chemistry*, ed. by N. A. Lange, New York, McGraw-Hill Book Company (various editions).

[4] *Fire Protection Handbook*, 13th edition, ed. by G. H. Tyron, Boston, National Fire Protection Institute (1969).

[5] *CRC Handbook of Tables for Applied Engineering Science*, ed. by Bolz and Tuve, Cleveland, CRC Press (1970).

the presence of a spark or flame. Such autoignition temperatures are not measures of fire hazard, but rather of the susceptibility of a material to destruction by elevated temperatures and represent temperatures above which a combustible material is not stable in air. Injection velocities necessary to achieve such temperatures are computed in the following section.

TEMPERATURE RISE BY RAPID DECELERATION

Rapid deceleration of a material from a high velocity causes its temperature to increase as kinetic energy is converted into internal energy. The deceleration also may disperse material into vapor form, or perhaps a fog or smoke of finely divided particles, where vaporization energy or increased surface energy is involved. Heat flow from warmed material to cooler impeding air also can occur.

It thus appears that the deceleration process for an injected material may be complicated, with many unknown factors. For screening purposes, however, it seems acceptable to take it that the major energy effect in the process is a simple conversion of kinetic energy to internal energy with increased temperature of the material. The velocity loss that causes the temperature of a material to reach the autoignition temperature is termed the critical injection velocity. Calculated values for this critical injection velocity are reported below for a variety of combustible materials.

The kinetic energy for a material is given in coherent units as the product of its mass and one-half the square of its velocity. Expressing mass in kilograms per mole of material, this becomes

$$KE = 1/2\left(\frac{M}{1000}\right) U^2 \qquad (1)$$

where KE is the kinetic energy in joules per mole, M the formula mass in grams per mole, and U the velocity in meters per second.

This kinetic energy, when converted to internal energy, generates a temperature rise Δt inversely proportional to the heat capacity of the system. Expressed algebraically per mole of material, $KE = C\Delta t$, where C is the molar heat capacity. Substituting into Equation (1) and solving for the velocity required to achieve a temperature rise from 25°C to a specified temperature t, in degrees Celsius,

$$U = 45 \sqrt{\frac{C}{M}} \sqrt{(t - 25)} \qquad (2)$$

Accompanying tables for critical injection velocities are based on Equation (2). They necessarily involve the molar heat capacities of the combustible materials of concern which, in general, are not known precisely. It appears however that for purposes here suitable approximations may well suffice, partially because only the square root of the item appears in the equation. These approximations are described in the following.

PARTIAL HEAT CAPACITIES

A reasonable estimate for the heat capacity of a material in a condensed phase can be obtained by the Kopp rule of additive partial values. Here the heat capacity per mole of a substance is taken as

$$C = \sum_i n_i c_i \qquad (3)$$

where c_i is the partial heat capacity for some particular atomic component and n_i the number of moles of atoms of that component. This approximation for heat capacity parallels that for formula mass. Partial heat capacities for atoms of concern in ordinary combustibles are given in Table 1, along with rounded values for the atomic masses.

TABLE 1. Partial Heat Capacities.

Element	Symbol	Atomic mass, g/mol	Partial heat capacity, J/mol-K
Hydrogen	H	1.0	9.6
Boron	B	10.8	11.3
Carbon	C	12.0	7.5
Oxygen	O	16.0	16.7
Fluorine	F	19.0	20.9
Silicon	Si	28.1	15.9
Phosphorus	P	31.0	22.6
Sulfur	S	32.0	22.6
All others	...	...	25.9

Estimates for heat capacities based on this table do not distinguish between constant pressure and constant volume conditions, but for

combustibles in a condensed phase the difference is small. The approximation also does not provide for the influence of temperature on heat capacity, nor for the difference between liquid and solid phases. But none of these effects is of key importance here so that Table 1 still provides reasonable estimates for ordinary combustibles.

Perhaps a more important drawback for the partial heat capacity values of Table 1 is a nonaccounting for the effects of vaporization. Vaporization requires energy, but the heat capacity of vaporized material is significantly lower. The calculations reported here proceed on the assumption that these effects approximately compensate.

CRITICAL VELOCITY FOR IGNITION BY DECELERATION

The critical injection velocity for ignition of a combustible material is that which assures that the material will actually ignite itself on complete deceleration when injected into a closed volume. Then an ensuing combustion gives an internal explosion with rapid pressure rise to the peak internal blast overpressure. This critical injection velocity is computed, from the autoignition temperature, by Equation (2).

Greater injection velocities than the critical can be expected to always cause an internal explosion. Lesser velocities than the critical also might cause an internal explosion but effects here depend on circumstances such as particle size, dispersion effects of the deceleration, the presence of a spark or flame, and undoubtedly other factors.

Critical velocities for injection of selected combustible materials using the heat capacity approximations of Table 1 have been computed and are reported as part of subsequent Tables 3 and 4. These velocities range from some few hundreds of meters per second for chemically active species, up to appreciably more than this for chemically stable species.

For air at 25°C the acoustic velocity is 345 m/s, closely, so that the critical velocities of the table are all supersonic with corresponding Mach numbers greater than unity, and usually in the order of 2 1/2 to 3. It is to be noted that such supersonic velocities would set up a shock wave ahead of a burning particle, and at very high velocities with associated high temperatures and short autoignition induction times the energy of this combustion could actually contribute to shock strength.

TEMPERATURE RISE BY MOLECULAR IMPACTIONS

An object moving through a gas with relative velocity U accumulates on its leading face a thin film of stagnate gas within which molecular

impacts have served to increase both the pressure and the temperature.[6] This increased temperature, the stagnation temperature t_o, in terms of bulk gas temperature t_1 is given as

$$t_o = t_1 + \frac{k-1}{2kR} U^2 \tag{4}$$

where k is the ratio of heat capacities for the gas and R its gas constant per unit mass; in this case, 8.314/0.029 J/kg-K. Solving Equation (4) for the velocity necessary to achieve a specified temperature t, °C, on the face of the object, and taking the bulk air temperature as 25°C,

$$U = 24 \sqrt{\frac{k}{k-1}} \sqrt{t - 25} \tag{5}$$

This equation is the basis for computation of a critical injection velocity for ignition by molecular impacts.

MEAN HEAT CAPACITY RATIOS FOR AIR

The ratio of the heat capacities in Equation (5) is based on the average heat capacity from a bulk air temperature of 25°C up to stagnation temperature. These ratios decrease with increasing stagnation temperature as the heat capacity itself increases. Values for these ratios as computed from experimental observations on heat capacity[7] are provided in Table 2 for both instantaneous values of the ratio at specified temperatures and for averages over a temperature range from 25°C. Also included are values for associated ratio $\sqrt{k/k-1}$ as called for in Equation (5). It can be noted that none of these is temperature-sensitive so that selected representative values might well suffice in many situations.

CRITICAL VELOCITY FOR IGNITION BY IMPACTION

Injection velocities required to raise the temperature of selected combustibles to their respective autoignition temperatures by molecular impaction have been computed by Equation (5) and are reported in Table 3 for a variety of flammable chemical compounds——and in Table 4 for

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[6] G. F. Kinney, *Explosive Shocks in Air*, New York, Macmillan (1962).

[7] Joseph H. Keenan and Joseph Kay, *Gas Tables, Thermodynamic Properties of Air*, New York, John Wiley & Sons (1948).

TABLE 2. Heat Capacity Ratios for Air.

Temp., °C	Heat capacity ratio, k		Mean, $(k/k-1)^{1/2}$
	at temperature	mean to 25°C	
25	1.400	...	1.871
200	1.389	1.396	1.878
400	1.367	1.386	1.894
600	1.347	1.375	1.914
800	1.330	1.365	1.934
1000	1.319	1.356	1.952
1200	1.311	1.348	1.967
1400	1.306	1.342	1.981

various combustible commercial products. Here, these may be compared with ignition velocities based on rapid deceleration—as computed by Equation (2). Comparing the two computed velocities, it can be seen that in general those for molecular impaction are less than those for rapid deceleration, but are of the same order of magnitude. The degree of correspondence obtained actually seems somewhat remarkable when the disparate methods of calculation are considered.

Comparing the physical basis for the two methods for computing critical injection velocity for ignition, that based on molecular impaction assumes a blunt face on an object that maintains its physical shape. In contrast, that based on rapid deceleration assumes only that injected material is brought to a halt by impeding air, or perhaps by confining walls, even though the material is widely dispersed. The actual mechanism for ignition by injection, of course, is not known because of items such as the effects of heat transfer to impeding air. Thus, both sets of reported critical ignition velocities must be regarded as somewhat speculative. They do, however, provide a solid basis for comparing different combustibles, and also a basis for subsequent refinement by suitable tests and experiments.

FLASH POINT TEMPERATURES

Sparks or open flames are common sources for ignition of combustible materials, but this ignition occurs only if the temperature of the combustible is sufficiently high. Otherwise, the combustion reaction does not propagate itself. Ignition is not a simple process. Thus, in many

TABLE 3. Ignition Velocities, Chemical Compounds

Compound	Formula	Auto-ignition Temp, °C	Critical injection velocity, m/s		Flash point, °C	Ignitability Velocity m/s
			Deceleration	Impaction		
1. Acetal	$C_6H_{14}O_2$	230	860	645	-20	0
2. Acetaldehyde	C_2H_4O	215	780	620	-30	0
3. Acetic acid	$C_2H_4O_2$	515	1200	1010	42	220
4. Acetic anhydride	$C_4H_6O_3$	395	1000	870	52	270
5. Acetone	C_3H_6O	580	1360	1080	-20	0
6. Acetylene	C_2H_2	315	870	770	Gas	0
7. Acrolein	C_3H_4O	285	850	730	-20	0
8. Acrylonitrile	C_3H_3N	480	1150	970	-5	0
9. Allyl alcohol	C_3H_6O	380	1090	860	22	0
10. Ammonia	NH_3	690	2070	1200	Gas	0
11. Amyl acetate, n	$C_7H_{14}O_2$	385	1100	860	25	0
12. Amyl acetate, iso	$C_7H_{14}O_2$	380	1100	860	30	140
13. Amyl alcohol, n	$C_5H_{12}O$	350	1120	820	40	240
14. Amyl alcohol, iso	$C_5H_{12}O$	350	1120	820	42	250
15. Amyl alcohol, sec	$C_5H_{12}O$	350	1120	820	30	140
16. Amyl chloride	$C_5H_{11}Cl$	300	1050	780	15	0
17. Aniline	C_6H_7N	700	1420	1200	70	370
18. Benzaldehyde	C_7H_6O	190	630	580	65	310
19. Benzene	C_6H_6	570	1200	1070	10	0
20. Benzoic acid	$C_7H_6O_2$	600	1160	1100	110	450
21. Bromobenzene	C_6H_5Br	690	1320	1200	65	320
22. Benzyl alcohol	C_7H_8O	435	1060	920	100	450
23. Biphenyl	$C_{12}H_{10}$	540	1120	1040	115	470
24. Butadiene	C_4H_6	430	1150	920	Gas	0
25. Butane, n	C_4H_{10}	440	1340	930	60	0
26. Butane, iso	C_4H_{10}	500	1440	1000	Gas	0
27. Butene-1	C_4H_8	410	1210	900	22	0
28. Butyl acetate	$C_6H_{12}O_2$	420	1150	900	30	130
29. Butyl alcohol, n	$C_4H_{10}O$	350	1120	820	35	200
30. Butyl alcohol, iso	$C_4H_{10}O$	430	1250	920	30	140

TABLE 3. Ignition Velocities, Chemical Compounds (Continued)

Compound	Formula	Auto-ignition Temp, °C	Critical injection velocity, m/s		Flash point, °C	Ignitability Velocity m/s
			Deceleration	Impaction		
31. Butyl alcohol, sec	$C_4H_{10}O$	410	1220	890	23	0
32. Butyl alcohol, tert	$C_4H_{10}O$	480	1325	970	10	0
33. Butyraldehyde	C_4H_8O	230	840	650	-7	0
34. Carbon disulfide	CS_2	110	60	410	-30	0
35. Chlorobenzene	C_6H_5Cl	640	1270	1140	30	110
36. Cresol, o	C_1H_8O	600	1250	1100	30	120
37. Cyclohexane	C_6H_{10}	280	940	720	-17	0
38. Decane, n	$C_{10}H_{22}$	250	950	680	46	290
39. Decalin	$C_{10}H_{18}$	260	920	690	60	360
40. Dichlorobenzene	$C_6H_4O_2$	650	1280	1150	65	320
41. Diethylene glycol	$C_4H_{10}O_3$	280	920	720	130	590
42. Ethyl acetate	$C_4H_3O_2$	425	1130	910	-5	0
43. Ethyl alcohol	C_2H_6O	410	1220	890	15	0
44. Ethylene glycol	$C_2H_5O_2$	415	1110	900	110	520
45. Ethylene oxide	C_2H_4O	430	1140	920	-20	0
46. Ethyl ether	$C_4H_{10}O$	185	790	570	-45	0
47. Formaldehyde	CH_2O	430	1080	920	Gas	0
48. Glycerin	$C_3H_8O_3$	390	1090	870	160	660
49. Heptane, n	C_7H_{16}	230	920	640	-4	0
50. Hexane, n	C_6H_{14}	250	970	680	-25	0
51. Hexane, iso	C_6H_{14}	280	1030	720	-30	0
52. Hexadecane, n (cetane)	$C_{16}H_{34}$	210	860	610	40	240
53. Methyl alcohol	CH_4O	470	1320	960	10	0
54. Methyl ethyl ketone	C_4H_8O	510	1290	1010	25	0
55. Methyl naphthalene, α	$C_{11}H_{10}$	530	1130	1030	70	340
56. Naphthalene	$C_{10}H_8$	550	1120	1050	80	360
57. Nitrobenzene	$C_6H_5NO_2$	490	1070	980	90	400
58. Nitroethane	$C_2H_5NO_2$	410	1120	890	90	460
59. Nitromethane	CH_3NO_2	420	1110	900	30	120
60. Nonane, n	C_9H_{20}	250	950	680	30	140

TABLE 3. Ignition Velocities, Chemical Compounds (Continued)

Compound	Formula	Auto-ignition Temp, °C	Critical injection velocity, m/s		Flash point, °C	Ignitability Velocity m/s
			Deceleration	Impaction		
61. Octane, n	C_8H_{18}	227	910	640	10	0
62. Octane, iso	C_8H_{18}	447	1310	940	15	0
63. Paraldehyde	$C_6H_{12}O_3$	240	830	660	15	0
64. Pentane, n	C_5H_{12}	300	1080	750	-30	0
65. Phenol	C_6H_6O	715	1320	1210	80	370
66. Propane	C_3H_8	500	1460	1000	Gas	0
67. Propyl acetate, iso	$C_6H_{10}O$	460	1180	950	5	0
68. Propyl alcohol, n	C_3H_8O	370	1150	840	25	0
69. Propyl alcohol, iso	C_3H_8O	400	1200	880	12	0
70. Propylene	C_3H_8	400	1400	950	Gas	0
71. Propyl ether, iso	$C_6H_{14}O$	445	1270	930	-30	0
72. Propylene glycol	$C_3H_5O_2$	420	1060	900	100	460
73. Stearic acid	$C_{18}H_{36}O_2$	395	1160	870	200	800
74. Styrene	C_8H_8	490	1100	980	30	115
75. Toluene	C_7H_8	540	1200	1040	5	0
76. Tetradecane	$C_{14}H_{30}$	200	830	600	100	550
77. Xylene, o	C_8H_{10}	480	1160	970	25	0
78. Xylene, m	C_8H_{10}	530	1220	1030	30	120
79. Xylene, p	C_8H_{10}	530	1220	1030	25	0
80. Zirconium (powdered)	Zr	290	990	740	...	...

TABLE 4. Ignition Velocities, Commercial Products

Combustible material	Auto-ignition Temp, °C	Critical injection velocity, m/s		Flash point, °C	Ignitability Velocity m/s
		Deceleration	Impaction		
1. Asphalt	485	880	980	200	540
2. Camphor	465	1240	960	80	440
3. Cleaning solvent, 60 °C flash	235	900	650	60	360
4. Creosote oil	340	920	800	75	370
5. Diesel fuel (typical)	245	920	670	45	270
6. Fuel Oil					
#1 (Kerosene-like)	230	880	640	40	240
#2 (Diesel fuel-like)	245	900	670	45	270
#4 (Standard heavy)	260	920	690	55	330
#6 (Bunker fuel)	400	1120	880	70	390
7. Gasoline					
73 octane	300	1020	750	-40	0
92 octane	390	1180	870	-40	0
100 octane	430	1240	910	-35	0
8. Jet Fuel					
JP-1	230	880	640	35	200
JP-4	250	930	680	40	240
9. Kerosene	230	880	640	43	260
10. Naphtha					
VM&P 50 °C flash	230	880	640	50	310
High flash	230	870	640	85	470
Coal tar	275	920	710	45	260
Safety (Stoddard)	245	900	670	40	240
11. Oil					
Castor	390	1150	870	230	860
Corn	390	1150	870	250	900
Cottonseed	345	1070	810	250	900
Gas oil	335	1060	800	200	800
Lard	445	1230	930	200	800
Linseed, boiled	340	1070	800	220	840
Lubricating, cylinder	490	1300	980	280	960
Olive	340	1070	800	275	950
Palm	350	1080	820	160	700
Paraffin oil	320	1060	780	190	800
Peanut	445	1230	930	280	960
Rosin oil	340	1070	805	130	620
Tung	455	1240	950	290	980
Whale	240	880	660	120	580

TABLE 4. Ignition Veclocities, Commercial Products (Continued)

Combustible material	Auto-ignition Temp, °C	Critical injection velocity, m/s		Flash point, °C	Ignitability Velocity m/s
		Deceleration	Impaction		
12. Petroleum ether	330	1090	790	-50	0
13. Pine Tar	335	1070	820	160	690
14. Tallow	400	1160	880	210	810
15. Turpentine	250	890	680	35	190
16. Wax					
Carnauba	440	1220	930	290	980
Paraffin	245	900	670	200	810

circumstances the required ignition temperature is generated in part by energy from the initiating spark or flame. Standardized laboratory procedures minimize errors introduced by this problem by arranging it so that the ignition source does not contribute materially to elevation of the temperature of the combustible. Of two types of such instruments, the simple open cup is suitable for the less volatile liquids, and a more complicated closed cup instrument that avoids the escape of vapors for the more volatile materials.

The minimum temperature at which a spark or flame can cause ignition of a combustible material is termed its flash point. Flash points for different combustible materials vary widely. For ethanol, a highly flammable material, the flash point is only 12°C (54°F) indicating that at ordinary room temperature this is potentially hazardous in case of fire or even in the presence of a low energy spark or flame. In contrast, the flash point for #2 fuel oil is about 65°C (149°F) indicating that the material is far less dangerous from the standpoint of ignition from a low energy source. Flash point temperatures are widely utilized in practice; for example, commercial kerosene by regulation should show a flash point not below 43°C (110°F).

Flash points are characteristics primarily of volatile liquids. For nonvolatiles such as coal dust or starch, the ignition process is much more difficult to describe. Thus, they may show no conventional flash point, but when finely divided and dispersed they are susceptible to ignition by a spark or a flame as many coal mine and grain elevator explosions attest. The ignition temperatures for such materials ordinarily are in the order of 300 to 600°C, not greatly different from those for volatile liquids. The energy required for their ignition however is some 20 to 50 times that needed for a flammable vapor.[4] Prudence indicates that any finely divided combustible material must be considered

dangerous and may "flash" even at room temperature or below. Such combustile dusts are not included in the tables presented here.

The observation that the more volatile combustibles show lower flash points has led to the rule of thumb that flash points can be estimated from boiling points, closely, by subtracting 100 and multiplying the difference by three-quarters (Celsius degrees). That is,

$$\text{Flash point, } °C = (3/4)(\text{Boiling point } °C - 100) \quad (6)$$

For mixtures such as gasoline which distill (boil) over a range of temperatures the initial boiling temperature applies. Not provided for by the equation is the effect of a so-called ignition improver such as amyl nitrate, various aldehydes, etc., which may drastically lower the flash point for a combustible. It should be apparent that the flash point is not a true property of a material, but only an instrument-dependent related parameter.

INJECTION VELOCITY FOR IGNITABILITY

An injection velocity which on rapid deceleration increases the temperature of a material to its flash point, produces a hazardous situation where any spark or flame in the vicinity can initiate an internal explosion. Tables 3 and 4 provide, in addition to autoignition temperatures, the observed flash points for a variety of combustible materials as given in various sources.[2-4] Also reported in the tables are the velocities which, on rapid deceleration, can raise the temperature of a material to its flash point where ignition might well occur. This injection velocity for ignitability is computed by Equation (2) using heat capacities as estimated by Equation (3). The injection velocity for ignitability for a material with a flash point below room temperature is, of course, zero.

The injection velocities for ignitability by a low energy spark or flame are well below these critical injection velocities for self-ignition where combustion occurs even in the absence of any initiating spark or flame.

EXPLOSION TEMPERATURES FOR EXPLOSIVES

An explosive such as TNT explodes spontaneously when exposed to elevated temperatures. The time required for this explosion to occur is temperature-dependent, and decreases markedly with increasing temperature.[8] Experimental measurement of such explosion time-temperature relationships is relatively simple if the equipment used avoids the

effects of temperature gradients and of intermediate temperatures. Explosion temperatures are known for many conventional chemical explosives,[9] selected values for which are included in Table 5 for the more or less standard exposure time of five seconds for self-explosion.

The temperature for self-explosion of an explosive material resembles in many ways that for the autoignition of a fuel, except for the presence of air, and that the induction time aspects of autoignition are partially masked by standardized laboratory methods.

For internal explosions with an explosive fuel, the standard exposure time of five seconds corresponds to a delayed ignition effect. Perhaps more important here is a much shorter time, one that corresponds to a prompt explosion. Such prompt explosions are taken as those which occur after an exposure time of only one-tenth second, temperature values for which are available for several standard explosives. For others, the temperature that corresponds to a prompt explosion can be estimated reasonably well on the basis that the Arrehenius activation energy for explosive decomposition is constant within a series of explosive chemical compounds.

INITIATION INJECTION VELOCITIES FOR EXPLOSIVES

Rapid deceleration of an explosive in a confined volume of air can well generate its explosion temperature. The velocities which on deceleration give this temperature, and so initiate explosions, have been computed by Equations (2) and (3) for selected explosives and are reported in Table 5. Those for prompt explosions correspond to ones that occur within one-tenth second and are based on experimental explosion temperature data where available. For explosives where data are more limited, a tenth-second explosion temperature was determined by extrapolation on an Arrehenius plot (log time versus reciprocal absolute temperature) when compared with data for such well-characterized explosives as TNT and tetryl. The velocities for initiation of a prompt explosion by the impaction method are also given in Table 5. In general, these are somewhat less than those for the deceleration mechanism.

Table 5 also provides velocities for delayed explosions, those which can be expected to occur after some five seconds. But even for the

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[8] Naval Weapons Center. *The Thermal Decomposition Characteristics of Explosives*, by C. A. Lind. China Lake, Calif., NWC, February 1968. (NOTS TP 2792, publication UNCLASSIFIED.)

[9] U. S. Army Materiel Command. *Properties of Explosives of Military Interest*. Washington, D.C., AMC Pamphlet 706-177 (1971).

TABLE 5. Initiation Velocity for Explosives

Explosive	Composition	Explosion temperature °C	Initiation velocity, m/s prompt explosion		Delayed Explosion
			Deceleration	Impaction	
1. Ammonium nitrate	NH_4NO_3	465	1340	1830	1240
2. Ammonium perchlorate	NH_4ClO_4	435	1250	1010	1140
3. Baratol	TNT 33%, $Ba(NO_3)_2$ 67%	385	1040	950	950
4. Baronal	TNT 35%, $Ba(NO_3)_2$ 50%, Al 15%	345	1800	800	920
5. Black powder	KNO_3 74%, C 16%, S 10%	430	1040	1000	950
6. Composition B	RDX 60%, TNT 40%	280	1180	1020	840
7. Composition C	RDX 88%, Plasticizer 12%	285	1040	840	900
8. Cyclonite (RDX)	$C_3H_6N_6O_6$	260	1070	890	840
9. Cyclotol 70/30	RDX 70%, TNT 30%	235	940	800	770
10. Diazodinitrophenol	$C_6H_2H_4O_5$	195	670	620	640
11. Diethyleneglycoldinitrate	$C_4H_8N_2O_7$	237	900	760	770
12. Dinitrotoluene	$C_7H_6N_2O_4$	310	960	870	850
13. Dynamite, low velocity	RDX 17%, TNT 68%, inerts 15%	480	1200	1060	1100
14. Explosive D	$C_6H_6N_4O_7$	320	1000	890	880
15. Glycol dinitrate	$C_2H_4N_2O_6$	250	920	800	790
16. Ethylenedinitramine (EDNA)	$C_2H_6N_4O_4$	190	850	670	730
17. H-6	RDX 45%, TNT 30%, Al 20%, inerts 5%	610	1400	1200	1310
18. HBX	RDX 40%, TNT 38%, Al 17%, inerts 5%	480	1250	1060	1150
19. HMX	$C_4H_8N_8O_8$	325	1040	860	960
20. Lead azide	PbN_6	340	1170	880	1080

TABLE 5. Initiation Velocity for Explosives (Continued)

Explosive	Composition	Explosion temperature °C	Initiation velocity, m/s prompt explosion		Delayed Explosion
			Deceleration	Impaction	
21. Lead Styphnate	$C_6H_3N_3O_9$ Pb	320	840	770	780
22. Mannitol hexa-nitrate	$C_3H_6N_6O_{18}$	230	730	530	600
23. Mercury fulminate	$C_2H_2O_2$ Hg	250	760	680	700
24. Nitrocellulose	13.5% Nitrogen	230	850	750	720
25. Nitroglycerine	$C_3H_5N_3O_9$	220	820	720	720
26. Nitroguanidine	$CH_4N_4O_2$	275	1030	780	940
27. NSX-demolition explosive	Nitrostarch (12.5%N) 50%, Barium nitrate 40%, inerts 10%	195	780	700	660
28. Octol 75/25	HMX 75%, TNT 25%	350	1070	900	970
29. Pentolite 50/50	PETN 50%, TNT 50%	220	820	740	700
30. PETN	$C_5H_8N_4O_{12}$	225	810	710	730
31. Picric acid (PA)	$C_6H_3N_3O_7$	320	940	880	830
32. Polyvinyl nitrate (PVN)	$(C_2H_3NO_3)_n$	265	900	780	800
33. Tetracene	$C_2H_8N_{10}O$	160	830	600	730
34. Tetryl	$C_7H_5N_5O_8$	255	890	800	770
35. Torpex	RDX 42%, TNT 40%, Al 18%	260	890	760	820
36. Trimonite	PA 90%, Nitro-naphthalene 10%	315	890	830	820
37. Trinitrotoluene	$C_7H_5N_3O_6$	475	1160	1070	1050
38. Tritonal 80/20	TNT 80%, Al 20%	470	1230	1110	1070

deceleration mechanism such velocities for delayed explosion may not be realistic, for in five seconds heat transfer to the cooler impeding air may drastically lower the temperature of the material. It also seems unlikely that temperatures generated by impaction could be maintained for this period of time by a material moving in a closed volume at several hundred meters per second. Hence, such initiating velocities are not reported.

Table 5 (for initiating velocities for explosives) includes two limiting values. One, a pair of two values for prompt ignition, are those injection velocities above which internal explosion effects seem assured. The other limiting value is for ignition at five seconds and represents a velocity below which ignition effect and consequent internal explosions can be erratic and might well depend on external effects such as the presence of some incidental spark or flame.

SUMMARY

The critical injection velocity for ignition of a combustible material is that velocity which raises its temperature to the ignition point. This temperature rise can result from molecular impaction effects on a blunt front face of a body, or from kinetic energy loss by rapid deceleration. Equations for each of these two mechanisms are developed, and critical injection velocities, as so computed are presented in tables for selected combustibles. Results for the two methods of computation are roughly in agreement, with a representative critical injection velocity being perhaps 800 to 1,000 m/s, corresponding to a Mach number of about 2 1/2 or 3.

Ignitability velocity is the velocity required to raise the temperature of a combustible material so that an external spark or flame can cause ignition. These ignitability velocities also have been computed, and in general are considerably less than those required for autoignition.

Injection velocities then can generate temperatures that cause prompt explosion of explosive materials, and also those for delayed explosions, have been computed and are presented in tabular form. These velocities are not greatly different from those required for ignition of ordinary combustibles.

The calculations here are all speculative in nature. Nevertheless, they provide a logical basis for the comparison of materials and also for modification and correction for inadequate assumptions in the simplified development leading to these reported results.

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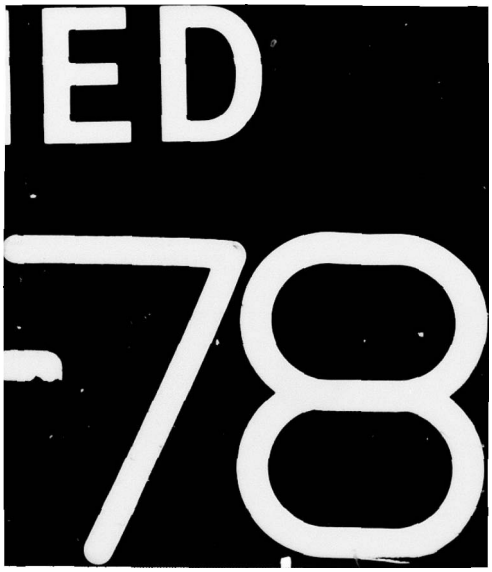
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